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(21) International Application Number: PCT/US92/01001 (22) International Filing Date: 27 February 1992 (27.02.92) (30) Priority data: 663,237 1 March 1991 (01.03.91) US (71) Applicant: CHEVRON RESEARCH AND TECHNOLOGY COMPANY [US/US]; Post Office Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventors: INNES, Robert, A. ; 15 Shannon Lane, San Rafael, CA 94901 (US). HOLTERMANN, Dennis, L. ; 55 Pennington Court, Crockett, CA 94525 (US). MULASKEY, Bernard, F. ; 18 Sherman Court, Fairfax, CA 94930 (US).	(74) Agents: TOUSLEE, Robert, D. et al.; Chevron Corporation, Law Department, Post Office Box 7141, San Francisco, CA 94120-7141 (US). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>	
(54) Title: LOW TEMPERATURE REGENERATION OF COKE DEACTIVATED REFORMING CATALYSTS (57) Abstract A process for regenerating a coke contaminated reforming catalyst comprising platinum on a molecular sieve, said process consisting essentially of contacting said catalyst with a halogen-free oxygen-containing gas at a temperature of less than 780 °F for a sufficient period of time such that the aromatization activity is restored to within 20 °F of the activity said catalyst possessed at the start of the previous run cycle.		

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LOW TEMPERATURE REGENERATION OF
COKE DEACTIVATED REFORMING CATALYSTS

BACKGROUND OF THE INVENTION

The subject of the present invention is a process for the regeneration of a hydrocarbon reforming catalyst which has been deactivated due to buildup of carbonaceous material on the catalyst. More specifically, the present invention provides a method for regenerating a coke deactivated reforming catalyst by a controlled low temperature carbon-burn procedure which results in the catalyst having activity, selectivity and stability characteristics approximating, or which are even better than, the catalyst prior to the buildup of carbon. The reforming catalysts intended to be regenerated by the process of the present invention comprise a molecular sieve material and platinum.

Platinum containing catalysts are widely used in the oil refining and petrochemical industries, and are particularly important in a reforming process where paraffins, olefins and naphthenes are converted to aromatic compounds. Conventional reforming catalysts typically include one or more metals, most typically platinum, dispersed on a base, and may also include a binding agent for adding physical support to the base, and chloride to provide an acidic function. Typically, the catalyst base is alumina, but recently molecular sieve based catalysts have been found to be effective for reforming reactions.

Catalytic compositions containing zeolites are well known in the industry and recently the use of L-zeolites in combination with other specified catalytic components have been found to be particularly preferred for reforming. The

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01 aromatic compounds produced by such a catalytic conversion
02 are valuable to a refiner due to their higher octane rating,
03 and may be recovered from the reforming product for further
04 processing and reaction in the petrochemical industries.
05 The L-zeolite catalysts are particularly effective for
06 converting C₆ and C₇ non-aromatic hydrocarbons which
07 normally boil between 125°F and 225°F, to benzene and
08 toluene.

09
10 In the reforming process, a hydrocarbon feedstock is passed
11 through a catalyst-containing reactor in the presence of
12 hydrogen at an elevated temperature. In the reactor and
13 upon contact with the reduced or activated catalyst, some of
14 the paraffins, olefins and naphthenes in the feedstock react
15 to form a more desired, higher octane aromatic product. In
16 the course of typical reforming operations, the catalysts
17 will typically become deactivated due to the deposition of
18 carbonaceous material or "coke" upon the catalyst, and/or
19 scinterring or poisoning of the catalytic metal particles.
20 In commercial practice, the deactivated catalyst will then
21 be regenerated by a process which may include as a step the
22 exposing of the catalyst to an oxygen containing gas at
23 elevated temperature (typically 950°F final burn
24 temperature) to burn the carbonaceous deposits accumulated
25 on the catalyst. However, prior to our present invention,
26 burning the coke off the catalyst at elevated temperatures
27 caused the catalytic metal to agglomerate, which
28 significantly lowered the activity and thus worsened the
29 performance of the catalyst. Consequently, specific steps
30 directed to the redispersion of the catalytic metal on the
31 base were necessary. The redispersion steps typically
32 comprise contacting the catalyst with a chloride containing
33 gas in the presence of oxygen and water vapor, and are well
34 known in the art.

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01 In U.S. Patent No. 4,493,901 issued January 15, 1985 to
02 Bernard et al., a method of regenerating a catalyst
03 comprising platinum and a non-acidic L-zeolite is described,
04 whereby the catalyst is subjected to a multi-step process,
05 the first step being exposure to a hydrogen environment,
06 followed by a carbon burn step, and then a calcination step
07 followed specifically by an oxychlorination step. The
08 regeneration method of Bernard et al. utilizes a hydration
09 step following the oxychlorination step. In the hydration
10 step, a quantity of water is added to the cooling air.

11 In U.S. Patent No. 4,810,683, issued March 7, 1989, to Cohn,
12 a method is described which utilizes a halogen or halogen
13 containing gas during the carbon burn step. The burning
14 step of the process of U.S. Patent No. 4,810,683 occurred
15 necessarily in the presence of a halogen or halogen
16 containing gas and at a temperature of from 300°C to 600°C.
17

18 U.S. Patent No. 3,986,982, issued October 19, 1976, to
19 Crowson et al., describes a method for regenerating a
20 deactivated platinum group metal-loaded zeolites by burning
21 off deposits on the catalyst with a stream of inert gas and
22 oxygen at a temperature controlled to a maximum of 550°C.
23 Example 1 shows a stepwise burn procedure to 530°C. The
24 water content was held at 100-130 ppm. This was followed by
25 treating with a stream of an inert gas containing from
26 0.5 to 20.0 vol% oxygen and from 5 to 500 ppmv chlorine as
27 chlorine gas. The resultant catalyst is purged to remove
28 residual oxygen and chlorine and then reduced with hydrogen.
29

30 U.S. Patent No. 4,359,400, issued November 16, 1982, to
31 G. R. Landolt et al., describes a process whereby
32 multimetallic platinum containing catalysts are contacted
33 with oxygen containing gas at elevated temperatures to burn
34

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01 off coke and then treated with dry, oxygen-free hydrogen
02 halide. The catalyst is then treated with Cl_2 containing gas
03 which is oxygen and water-free.

04 U.S. Patent Number 4,719,189, issued January 12, 1988 to
05 A. S. Krishnamurthy describes a process for rejuvenating a
06 coke-deactivated noble metal containing zeolite catalyst.
07 The process comprises contacting the catalyst with a mixture
08 of oxygen and sulfur dioxide, followed by catalyst
09 reduction. Temperatures from 752-840°F are preferred.
10

11 U.S. Patent No. 4,645,751, issued February 24, 1987, to
12 S. B. McCullen et al., describes a process for rejuvenating
13 a highly silicious (silica-alumina ratio of at least 20)
14 Pt zeolite catalyst wherein the Pt has become agglomerated.
15 The agglomerated catalyst is first reduced with hydrogen.
16 Following reduction the catalyst is treated with hydrogen
17 chloride and oxygen in an inert gas carrier at 400-450°C.
18

19 U.S. Patent No. 4,752,595, issued June 21, 1988, to
20 S. B. McCullen et al., describes a process for regenerating
21 a noble-metal containing zeolite catalyst. The process
22 consists of a coke burn step followed by a low temperature
23 reduction step (212-482°F) Oxidizing conditions for the coke
24 burn include temperatures ranging from 392-1004°F,
25 preferably 752-950°F.
26

27 U.S. Patent No. 4,657,874, issued April 14, 1987, to
28 W. S. Borghard et al., describes a method where Pt on a
29 highly silicious zeolite is redispersed. The process
30 comprises a coke burn followed by oxychlorination. The
31 oxygen burn step is done under conditions that are
32 sufficiently mild to prevent any alteration in the crystal
33 structure of the zeolite. Example 6 uses a temperature of
34

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01 850°F. This is then followed by treating with a stream of
02 inert gas containing 6 to 15 Torr of chlorine gas and water
03 vapor such the molar ratio of water to chlorine gas is
04 between 0.01 and 2.0. Oxygen may also be present. The
05 rejuvenation is typically carried out at 450°C (842°F).

06 U.S. Patent No. 4,851,380, issued July 25, 1989, to
07 D. A. Van Leirsburg et al., describes a process for
08 regenerating a sulfur contaminated reforming catalyst. The
09 process includes a platinum agglomeration step which can be
10 accomplished by contacting the catalyst with O₂ between
11 800°F and 1200°F and an oxychlorination step. Pt
12 redispersion by contacting an agglomerated catalyst with
13 carbon monoxide and a sulfur free halogen acid gas.
14

15 U.S. Patent No. 4,855,269, issued August 8, 1989, to
16 D. H. Mohr, discloses a platinum redispersion method
17 comprising a wet oxychlorination step, followed by a
18 nitrogen purge, followed by reduction.
19

20 U.S. Patent No. 4,914,068 issued April 3, 1990, to
21 V. R. Cross, describes a process for the improved retention
22 of the platinum dispersion following oxychlorination if the
23 catalyst is cooled to 430°C or preferably less than 375°C
24 prior to start of reduction. Coke was burned off the
25 catalyst at 510°C prior to reduction.
26

27 Unfortunately, the presence of halogens such as chlorine or
28 flourine or their compounds during regeneration results in
29 the formation of corrosive by-products such as HCl and
30 NH₄Cl. These compounds can cause damage to equipment used
31 in the reforming process such as heat exchangers, liquid/gas
32 separators and reactor internals. The halogen containing
33 compounds and their products necessary for platinum
34

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01 redispersion are highly toxic as well. Therefore, it is
02 highly desirable to have available a catalyst regeneration
03 procedure that does not include the use of a halogen
04 containing gas.

05 Prior to our discovery of the regeneration process of the
06 present invention, it was thought by those skilled in the
07 art that platinum metal agglomeration was an unavoidable
08 result of the reforming process and subsequent coke
09 burn-off. Consequently, it was believed that platinum
10 redispersion using halogen containing compounds was a
11 necessary step in the regeneration procedure. A
12 regeneration method which does not require halogens has long
13 been desired.
14

15 SUMMARY OF THE INVENTION
16

17 The present invention relates to a halogen-free process to
18 regenerate a coke contaminated catalyst comprising platinum
19 on a molecular sieve support which process comprises
20 contacting said catalyst with an oxygen-containing gas at a
21 temperature of from 300°F to no more than about 780°F. More
22 particularly, it relates to a process to regenerate a coke
23 contaminated catalyst comprising contacting said catalyst
24 with a halogen-free oxygen-containing gas at a maximum
25 temperature of less than 780°F for a sufficient period of
26 time such that the aromatization activity is restored to
27 within 20°F of the aromatization activity the catalyst
28 possessed at the start of the previous run cycle. By the
29 term "aromatization activity" we mean the extrapolated start
30 of run temperature where the run conditions and the feed as
31 well as the aromatics yield are substantially the same as in
32 the previous run cycle. By the practice of the present
33 invention, the platinum on the catalyst remains sufficiently
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01 dispersed on the support to allow for an activity change of
02 not more than 20°F upon termination of the regeneration
03 procedure, and return of the catalyst to hydrocarbon
04 conversion service. Thus, the catalyst aromatization
05 activity is based upon the temperature needed to achieve a
06 desired constant aromatics production. Typically, we have
07 controlled our process to about 40 to 42 wt.% aromatics in
08 the product, although other values may be set, in other
09 circumstances. Regeneration by the process of the present
10 invention results in a catalyst which has an aromatization
11 activity, as defined above, which is within 20°F of the
12 temperature needed in the previous run to achieve the same
13 constant aromatics production.

14 Among other factors, we have found that by limiting the
15 ultimate temperature in the carbon burn regeneration
16 procedure to a maximum temperature of less than 780°F,
17 preferably between 600°F to 750°F the catalyst may be
18 restored to an activity very close to that of the fresh
19 catalyst, without requiring a metal re-dispersion step. It
20 is further preferred the carbon burn be initiated at a
21 temperature of less than about 500°F and further that the
22 recycle gas be dried to achieve a water concentration in the
23 recycle gas of less than 100 ppm water, prior to the recycle
24 gas entering the reforming reactor train.

25
26 We have found that by avoiding addition of a halogen or
27 halogen containing gas during or after the carbon burn
28 procedure, plant deterioration due to stress cracking and
29 corrosion is minimized. Further, prior to our present
30 invention, it was common practice to circulate soda ash or
31 morpholine solutions through effluent heat exchangers,
32 transfer lines, and liquid-gas separators during the
33 regeneration of reforming catalyst in order to prevent
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01 corrosion due to chlorides. The need to use corrosion
02 inhibitor solutions is eliminated when regenerating
03 reforming catalyst by the method of the present invention.

04 In general, the art teaches away, i.e., describes high
05 temperature burn procedure followed by redispersion step or,
06 burn/redispersion combined. We have now, surprisingly,
07 found that if the coke burn and reduction are both done at
08 low temperatures and with low concentration of water, the
09 regenerated catalyst has excellent activity and unexpectedly
10 long life.
11

12 Surprisingly, we have also found that the rate of
13 deactivation or "fouling rate" of the regenerated catalyst
14 decreases following the application of the regeneration
15 process of the present invention. Thus, a catalyst
16 regeneration procedure was discovered in which noble metal,
17 does not appreciably agglomerate; eliminating the need for a
18 redispersion step, which are among the advantages of using
19 the present regeneration method on a Pt containing molecular
20 sieve type catalyst.
21

22 DETAILED DESCRIPTION OF THE INVENTION

23
24 As explained in the summary section above, the present
25 invention is a procedure for regenerating reforming
26 catalysts, comprising platinum on a molecular sieve support.
27

28 By the term "reforming" we mean the process of converting
29 paraffins, naphthenes or olefins to aromatic hydrocarbons
30 via hydrodecyclization or dehydrogenation. Feeds useful in
31 reforming typically include hydrocarbons having from six to
32 eleven carbon atoms, but these feeds can also include
33 narrower cuts, such as a C₆ to C₇ cut. Indeed, the
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01 reforming catalysts that can be regenerated by the process
02 of this invention can be used to make chemicals as well as
03 gasoline components. For example, benzene, toluene or
04 mixtures thereof can be produced by reforming hydrocarbons
05 having six to seven carbon atoms.

06 The catalysts advantageously regenerated by the method of
07 this invention comprise platinum on a molecular sieve
08 support. Molecular sieves are defined as porous materials
09 which exhibit the property of acting as sieves on a
10 molecular scale. The molecular sieves of most interest for
11 catalysis are those which have uniform pore sizes in the
12 4.2 to 15 Angstrom diameter range, particularly crystalline
13 materials of the aluminophosphate, aluminosilicate, and pure
14 silica types. The aluminosilicate molecular sieves include
15 zeolites and certain modified clays.
16

17 Examples of aluminophosphate molecular sieves include
18 ALPO-5, ALPO-11, ALPO-31, ALPO-34, and ALPO-41, as well as
19 isostructural materials containing silicon, cobalt,
20 manganese, magnesium, iron, chromium, titanium, or other
21 elements as part of the crystalline framework. Zeolite
22 molecular sieves of particular interest include zeolite
23 types X, Y, and L, mordenite, ZSM-5, ZSM-12, ZSM-20, SSZ-25,
24 SSZ-26, and beta zeolite. Examples of modified clays with
25 molecular sieving properties include pillared bentonites and
26 hectorites. Silicalite and SSZ-24 are examples of molecular
27 sieves composed of substantially silica. Silicalite has the
28 same crystal structure as ZSM-5 except that substantially
29 all of the aluminum atoms have been replaced with silicon
30 atoms. SSZ-24 is the all-silica structural analog of
31 ALPO-5.
32

33

34

Catalyst Description

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In copending Application Serial No. 496,119, assigned to the assignee of the present invention and entirely incorporated by reference herein, an intermediate pore size crystalline silicate having a silica to alumina ratio of preferably at least 500, is described. We have found the present catalyst regeneration process may be advantageously used to regenerate the intermediate pore size crystalline silicate catalyst, and that the present process may also be advantageously applied to a mixed catalyst system comprising the intermediate pore size crystalline silicate described in copending Application Serial No. 496,119.

A preferred catalyst to regenerate by the process of this invention comprises platinum on an alkaline earth or alkali metal exchanged, L-zeolite. It is especially preferred that this catalyst be protected from sulfur poisoning during its use in reforming, so that the catalyst is never contacted with more than 100 ppb by weight sulfur in the feed. This can be accomplished by using a sulfur converter/sorber system as described in U.S. Patent No. 4,925,549 to Robinson et al. The regeneration process of this invention is especially effective on substantially sulfur free catalyst.

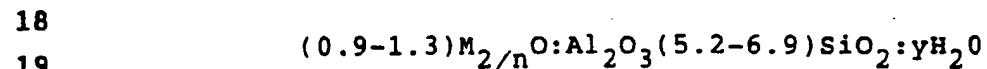
In addition to platinum, the catalysts regenerated by the present invention may contain elements such as rhenium, tin, germanium, iridium, copper, iron, cobalt, nickel, and titanium which in certain cases may improve catalyst selectivity or stability. For naphtha reforming, it is desirable that the molecular sieve catalyst have a low acidity. Acid sites may be neutralized by ion exchange with alkali ions such as lithium, sodium, potassium, cesium and rubidium ions or alkaline earth ions such as calcium,

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01 magnesium, strontium, and barium. With zeolites, low
02 acidity may also be achieved by substituting boron for
03 aluminum in the zeolite framework; for example, boron
04 substituted beta zeolites or by using a zeolite with a
05 silica/alumina ratio greater than 500.

06
07 The present invention has been found to be particularly
08 effective when applied to large-pore zeolites. Large-pore
09 zeolites are defined as zeolites having an effective pore
10 diameter of between 6 and 15 Angstroms. Among the
11 large-pore zeolites which have been found to be useful as
12 reforming catalysts, L-type zeolites are the most important.
13 Other important zeolites include X-zeolites, Y-zeolites,
14 mordenites, and zeolite beta.

15
16 A typical composition of L-type zeolites, expressed in terms
17 of mole ratios of oxides, may be represented as follows:



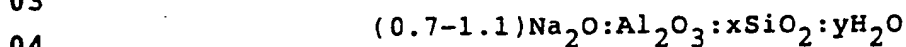
20
21 wherein M designates a cation, n represents the valance of
22 M, and y may be any value from 0 to 9. Zeolite L, its X-ray
23 diffraction pattern, its properties and method for its
24 preparation are described in detail in U.S. Patent
25 No. 3,216,789 which is hereby incorporated by reference.
26 The true formula may vary without changing the crystalline
27 structure. For example, the mole ratio of silicon to
28 aluminum (Si/Al) may vary from over a range which is
29 typically 1.5 to 3.5, but may be higher. The barium
30 exchanged form of zeolite L is particularly preferred as
31 described, for example, in U.S. Patent Nos. 4,434,311 and
32 4,547,472.

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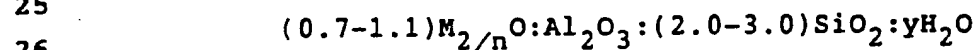
01 The chemical formula for zeolite Y expressed in terms of
02 oxide molar ratio may be written as:



05
06 wherein x is a value between 3 and 6, and y may be a value
07 up to 9. Zeolite Y has a characteristic X-ray diffraction
08 pattern which may be employed with the above formula for
09 identification. Zeolite Y is described in more detail in
10 U.S. Patent No. 3,130,007. U.S. Patent No. 3,130,007 is
11 hereby incorporated by reference herein to show a zeolite
12 useful in the present invention.

13
14 More recent patents disclose high silica/alumina versions of
15 zeolite Y produced by steaming and/or chemical extraction
16 which removes aluminum from the framework of the originally
17 synthesized zeolite. Y-zeolites with framework
18 silica/alumina ratios as high as 50:1 or higher may be
19 prepared by these methods, and are useful supports for the
20 reforming catalysts regenerated by the method of the present
21 invention.

22
23 Zeolite X is a synthetic crystalline zeolitic molecular
24 sieve which may be represented by the formula:



27
28 wherein M represents a metal, particularly alkali and
29 alkaline earth metals, n is the valence of M, and y may have
30 any value up to about 8 depending upon the identity of M and
31 the degree of hydration of the crystalline zeolite.
32 Zeolite X, its x-ray diffraction pattern, its properties and
33 method for its preparation are described in detail in
34 U.S. Patent No. 2,882,244, which is hereby incorporated by

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01 reference in its entirety to show a zeolite useful in the
02 present invention.

03
04 Zeolite beta is a known synthetic crystalline
05 aluminosilicate originally described in U.S. Patent
06 Nos. 3,308,069 and RE 28,341 to which reference is made for
07 further details of this zeolite, its preparation and
08 properties. These references describe the composition of
09 zeolite beta in its as-synthesized form as follows:

10
11
$$[XNa(1.0 \pm 0.1 - X)TEA]AlO_2 \cdot Y(SiO_2 \cdot W H_2O)$$

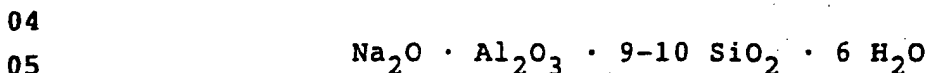
12
13 where X is less than 1, preferably less than 0.75, TEA
14 represents tetraethylammonium ion, Y is greater than 5 and
15 less than 100, and W is up to about 4, depending on
16 the condition of dehydration and on the metal cation
17 present. These references also teach that the sodium ion
18 may be replaced by another metal ion using ion exchange
19 techniques. Subsequent publications such as European Patent
20 Applications Nos. 95,304; 159,846; 159,847; and 164,939 have
21 broadened the definition of zeolite beta to include
22 materials prepared using templating agents other than
23 tetraethylammonium hydroxide and materials having a Si/Al
24 ratio greater than 100. Also the zeolite described in
25 European Patent Application No. 55,046 ("Nu-2") and British
26 Patent Application No. 2,024,790 ("Borolite B") have
27 structures and X-ray diffraction patterns similar to that of
28 zeolite beta and are included within the scope of the term
29 "zeolite beta" as used herein.

30
31 Mordenite is a commercially available zeolite which occurs
32 in nature and has also been synthesized. Both "small port"
33 and "large port" mordenites have been synthesized. The
34 "large port" form is preferred for catalysis and is

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01 described in "Zeolite Molecular Sieves" by Donald W. Breck,
02 published by John Wiley and Sons. A typical oxide
03 composition is



06
07 The silica/alumina ratio may be increased by extracting
08 alumina using various chemical and thermal methods similar
09 to those employed with zeolite Y.

10
11 The percentage of platinum in the catalyst is between 0.1%
12 and 10%, the lower limit corresponding to minimum practical
13 catalyst activity and the upper limit to roughly the maximum
14 possible platinum utilization. Preferably, the catalyst
15 contains between 0.2 and 5.0 percent platinum. Group VIII
16 metals are introduced into a large-pore zeolite during
17 synthesis, impregnation or ion exchange in an aqueous
18 solution of an appropriate metal salt. If it is desired to
19 introduce two Group VIII metals onto the large-pore zeolite,
20 the operation may be carried out simultaneously or
21 sequentially.

22
23 By way of example, platinum can be introduced by
24 impregnating the large-pore zeolite with an aqueous solution
25 of tetrammineplatinum (II) nitrate $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$,
26 tetrammineplatinum (II) chloride $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$, or
27 diammineplatinum $[\text{Pt}(\text{NH}_3)_2](\text{NO}_2)_2$. In an ionic exchange
28 process, platinum can be introduced by using cationic
29 platinum complexes such as tetrammineplatinum (II) nitrate.

30
31 A binder may be used in the preparation of the catalysts.
32 An inorganic oxide is used as a matrix to bind the
33 large-pore zeolite. This binder can be a natural or a
34 synthetically produced inorganic oxide or combination of

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01 inorganic oxides. Typical inorganic oxide binders which can
02 be used include clays, alumina, silica or mixtures thereof.
03 Preferable binders are alumina, silica, or mixtures thereof.
04 Acidic sites on the binder are preferably exchanged by
05 cations which do not impart strong acidity (such as sodium,
06 potassium, rubidium, cesium, calcium, strontium or barium).

07
08 After the desired metal or metals have been introduced, the
09 catalyst is typically calcined in air and then reduced in a
10 hydrogen environment.

11
12 The regeneration process of the present invention may be
13 useful on catalysts in the physical form of extrusions,
14 spheres, pills, pellets, granules, broken fragments, or
15 various other shapes known in the art.

16 Catalyst Use and Contamination

17
18 The reforming catalysts regenerated by the process of the
19 present invention are used for aromatization of C_6 to C_{11} ,
20 preferably C_6 and C_7 non-aromatic hydrocarbons.
21 Accordingly, a hydrocarbon feedstream which comprises a C_6
22 to C_{11} paraffin, olefin, or naphthene, is contacted with the
23 catalyst at aromatization conditions. Aromatization
24 conditions typically include an absolute pressure of from
25 about 0.5 to about 50.0 atmospheres, with the preferred
26 pressure being from about 1.0 to about 10.0 atmospheres, a
27 temperature of from about 800°F to about 1200°F, preferably
28 800°F to 1050°F, and a liquid hourly space velocity of from
29 between about 0.1 to about 10 per hour. Preferably,
30 hydrogen is employed in the process. When present, hydrogen
31 may be circulated at a rate of from about 1.0 to about 10.0
32 moles of hydrogen per mole of hydrocarbon in the hydrocarbon
33 feedstream. Feed streams entering the reforming reactors
34

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01 should be low enough in sulfur and water to prevent catalyst
02 deactivation by sulfur poisoning or platinum sintering.

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Catalyst Regeneration Method

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The gradual accumulation of coke and other deactivating carbonaceous deposits on the catalyst will eventually reduce the activity of the catalyst and selectivity of the aromatization process. Typically, catalyst regeneration becomes desirable when from about 0.5 to about 3.0 wt. % or more of carbonaceous deposits are laid down upon the catalyst. At this point, it is typically necessary to take the hydrocarbon feedstream out of contact with the catalyst and purge the hydrocarbon conversion zone with a suitable gas stream. The catalyst regeneration method of the present invention is then performed either by unloading the catalyst from the conversion zone and regenerating in a separate vessel or facility or performing regeneration in-situ. Alternatively, the catalyst may be continuously withdrawn from the reactor for regeneration in a separate vessel, to be returned to the reactor as in a Continuous Catalytic Reformer.

According to the catalyst regeneration method of the present invention, the essential step of the method incorporates a lower temperature carbon burn step. The lower temperature carbon burn step involves contacting the deactivated catalyst with a gaseous mixture of oxygen and an inert gas. The oxygen is typically derived from air and an inert gas serves as a diluent, such that oxygen concentration is from about 21 mole % oxygen to a lower limit which for the practice of the present invention may be as low as 0.1 mole % oxygen. The practice of the present invention is not limited to use of air, however, and higher levels of oxygen

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01 may be used in methods where oxygen is supplied in a more
02 pure form such as from cylinders or other containing means.
03 Typical inert gases useful in the low temperature carbon
04 burn step may include nitrogen, helium, carbon dioxide, and
05 like gases or any mixture thereof; nitrogen being preferred.
06 The regeneration gases should be substantially sulfur-free
07 as they enter the reactor, and preferably contain less than
08 100 part per million by volume water. Because the oxygen
09 content determines the rate of burn, it is desirable to keep
10 the oxygen content low so as not to damage the catalyst by
11 overheating and causing metal agglomeration, while still
12 conducting the carbon burn step in a manner that is both
13 quick and effective. We have found it desirable to keep the
14 oxygen level in the inlet to the regeneration vessel between
15 0.2 to 4.0 mole % during the practice of the present
16 invention to avoid thermal damage to the catalyst, and still
17 allow for the regeneration process to be accomplished in a
18 reasonable amount of time.

19
20 The low temperature carbon burn process of the present
21 regeneration method occurs at a temperature of between 300°F
22 to 780°F. Other conditions present during the low
23 temperature carbon burn step include a pressure sufficient
24 to maintain the flow of the gaseous oxygen containing
25 mixture through the catalyst zone such as a pressure of
26 between about 1.0 to 50.0 atmospheres and preferably from
27 about 2 to about 15 atmospheres, and a gas hourly space
28 velocity of about 100 to about 10,000 per hour, with a
29 preferred value of about 500 to about 5,000 per hour.

30
31 The regeneration method of the present invention is
32 performed in a halogen-free environment. By halogen-free,
33 we mean that chlorine, fluorine, bromine, or iodine or their
34 compounds including for example, hydrogen chloride, carbon

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01 tetrachloride, ethylene dichloride, propylene dichloride;
02 are not added at anytime during the catalyst regeneration
03 process.

04 It is desirable to keep water levels low during the
05 reforming reactions and during the regeneration procedure.
06 This is especially true when temperatures are above 700°F.
07 Although short periods of time (several minutes) at water
08 levels as high as saturation can be tolerated at
09 700°F and higher, it is desirable to avoid this high a water
10 level.
11

12 A preferred embodiment of the present invention includes the
13 use of a dryer in combination with flowing at least a
14 portion of the combustion gas resulting from the contacting
15 of the catalyst with the oxygen containing gas to a dryer
16 and recycling the dried combustion gas to the catalyst zone.
17 We have found that drying the recycle gas further reduces
18 catalytic metal agglomeration, resulting in a more active
19 regenerated catalyst. It is preferred that water in the
20 recycle gas be reduced to less than 100 ppmv, more
21 preferably less than 10 ppmv, prior to the gas being
22 recirculated to the catalyst zone. We have found results to
23 be best when a fresh dryer is employed just prior to the
24 beginning of and throughout the coke-burn step.
25

26 In the preferred embodiment of the present invention, the
27 low temperature carbon burn step results in removing most of
28 the carbonaceous material from the catalyst while leaving an
29 amount of from between 0.1 to about 0.5 wt.% carbon on the
30 catalyst. Although the present invention is not limited by
31 any theory of operation, one possible explanation of the
32 resulting improved catalyst performance is that the small
33 amount of carbon remaining on the catalysts locates at the
34

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01 acid sites, and thus significantly decreases the fouling
02 rate of the regenerated catalyst. Surprisingly, we have
03 also found the yield of C_5+ product selectivity to increase
04 slightly after a first regeneration of the catalyst.

05
06 Further, in another preferred embodiment of the present
07 invention, the first reactor inlet temperature is increased
08 during the carbon burn in a step-wise fashion over a period
09 of about one to five days from an initial temperature of
10 less than 500°F, preferably between 300°F and 500°F to
11 achieve a final peak catalyst bed temperature of less than
12 780°F, preferably between about 600°F and 750°F.

13
14 The oxygen concentration at the first reactor inlet should
15 be controlled in the process of the present invention so as
16 to limit exotherms and high moisture levels due to
17 hydrocarbon combustion. Therefore, in the practice of a
18 preferred embodiment of the present invention, the oxygen is
19 maintained at a level between about 0.2 mole % and
20 2.0 mole % in the oxygen containing gas throughout the
21 carbon burn-off step. During the initial stages of the
22 burn, it is preferred the oxygen level be maintained at a
23 level between 0.2 and 0.5 mole %. As the rate of burn
24 subsides, oxygen levels may be increased to between 0.5 and
25 4.0 mole %.

26
27 The resulting regenerated catalyst with a portion of
28 carbonaceous material burned off is thereafter typically
29 cooled to about 500°F and purged with nitrogen or another
30 inert gas to displace the oxygen and any water therefrom.
31 The exit gas is easily monitored to determine when the
32 catalyst zone is substantially free of oxygen and water.

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01 After the low temperature carbon burn-off and purge, the
02 catalyst is activated by treatment with hydrogen. In the
03 initial reduction step, the catalyst is contacted with a
04 hydrogen containing stream at a temperature of from about
05 300°F to about 700°F for a period of at least of about 0.1
06 to about 10.0 hours. Preferred conditions for the reduction
07 step are from about 400°F to about 600°F for a period from
08 about 0.1 to about 2.0 hours. The pressure and gas rates
09 utilized in the reduction step are preferably very similar
10 to those above described in the low temperature carbon burn
11 step. Following the initial reduction, the catalyst may be
12 further reduced and dried by circulating a mixture of inert
13 gas and hydrogen while raising the temperature to between
14 900 and 1000°F. In the reduction step, metallic components
15 are returned to their elemental state and the resulting
16 regenerated catalyst possesses activity, and selectivity
17 characteristics quite similar to those occurring in a fresh
18 catalyst. Additionally, we have found the regenerated
19 catalyst has improved stability, as measured by a decreased
20 fouling rate. When iron oxides are present on the catalyst
21 or in the piping, it is desirable to use at least a 4:1 mole
22 ratio of nitrogen to hydrogen during the reduction and
23 dryout procedure, in order to limit the formation of NH_3 to
24 less than 200 ppmv.

25
26 After completing the reduction step, the temperature is
27 lowered to 800°F or less. The reforming process in which the
28 catalyst is employed may be resumed by charging the
29 hydrocarbon feedstream to the catalyst zone and adjusting
30 the reaction conditions to achieve the desired conversion
31 and product yields.

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01 The following examples are intended to further exemplify the
02 invention, and are not intended to limit the invention in
03 any way.

04
05 LOW TEMPERATURE REGENERATION

06
07 EXAMPLE I

08
09 Pretreatment and Composition of Naphtha Feedstock

10
11 A hydrocarbon feedstock was hydrotreated and dried to remove
12 sulfur, oxygen, and water. The treated feed was stored
13 under nitrogen to keep it substantially free of water and
14 oxygen. The sulfur content of the hydrotreated feed was
15 about 0.1 ppmw. A gas chromatographic analysis showed the
16 following composition.

17		LV%
18		
19	i-pentane	0.0
20	n-pentane	0.5
21	2,2-dimethylbutane	2.2
22	2,3-dimethylbutane	3.5
23	2-methylpentane	17.9
24	3-methylpentane	14.5
25	n-hexane	20.0
26	2,2-dimethylpentane	1.3
27	2,4-dimethylpentane	1.7
28	2,3-dimethylpentane	2.8
29	2-methylhexane	7.5
30	3-methylhexane	8.5
31	n-heptane	4.5
32	c ₈ ⁺ paraffins	2.1
33	cyclopentane	1.2
34	methylcyclopentane	4.9
	cyclohexane	2.0
	methylcyclohexane	0.5
	other C6 - C7 naphthenes	1.7

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01	benzene	0.2
	toluene	0.7
02	ethylbenzene	0.2
03	heavies	1.6

EXAMPLE IIFirst Run Cycle Starting with Fresh Catalyst

Eighty cubic centimeters of fresh reforming catalyst were charged to a one-inch diameter tubular reactor. The catalyst comprised platinum on barium exchanged L-zeolite and a binder. The reactor was installed in a naphtha reforming pilot plant inside a three-zone electric furnace. Catalyst bed temperatures were measured by six equally spaced thermocouple points located from the top to the bottom of the catalyst bed in an axial thermowell. The pilot plant was purged and pressure tested with nitrogen, depressured, then pressured to 100 psig with a blend of 1.0 % oxygen in nitrogen and the recycle compressor started. The reactor effluent passed through a chilled liquid-gas separator, a moisture analyzer, a dryer containing 4 A molecular sieves, a compressor, a mass flowmeter, and back to the reactor. The gas circulation rate was adjusted to 0.7 standard liters per minute. A small amount of the recycle gas was allowed to bleed off the recycle loop and makeup oxygen/nitrogen blend was fed from a cylinder.

The catalyst was dried by circulating the oxygen/nitrogen blend and heating the to 500°F. The temperature was held at 500°F until the reactor effluent contained less than 300 ppm water. The furnace temperature was then raised to 600°F and held until water in the reactor effluent again was less than 300 ppm. Finally, the temperature was raised to 700°F and held until the reactor effluent contained less than 100 ppm

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01 water. The reactor was cooled to 500°F and he
02 oxygen/nitrogen makeup gas replaced with dry nitrogen. The
03 pilot plant was purged of oxygen and the pressure adjusted
04 to 70 psig with the compressor continuing to operate at the
05 same setting.

06 Catalyst reduction was initiated by switching the makeup gas
07 from nitrogen to hydrogen and pressuring from 70 psig up to
08 100 psig. The compressor setting was then readjusted to
09 again obtain a circulation rate of 0.7 standard liters per
10 minute. After holding at 500°F for an hour, the reactor
11 furnace reactor temperature was raised to 700°F at rate of
12 50°F/h. The temperature was held at 700°F until water in
13 the reactor effluent was less than 300 ppmv and then raised
14 to 800°F at 50°F/h. When moisture in the reactor effluent
15 again fell below 300 ppmv, the temperature was raised to
16 900°F and held until water in the reactor effluent was less
17 than 100 ppmv. The furnace temperature was then lowered to
18 800°F and preparations were made for naphtha feed
19 introduction. This included putting a sulfur
20 converter/sorber reactor on-line in the recycle loop between
21 the naphtha feed introduction point and the reforming
22 reactor. The purpose of the sulfur converter/sorber was to
23 reduce sulfur compounds in the feed entering the reforming
24 reactor to below 5 ppbv.

25
26 The naphtha feed from Example I was fed at a rate of
27 128 mL/h corresponding to a liquid hourly space velocity
28 (LHSV) of 1.6 volumes of feed per volume of catalyst per
29 hour. Pressure was controlled at 100 psig by allowing
30 product hydrogen gas to exit the recycle loop through a
31 backpressure regulator. The product hydrogen stream was
32 analyzed and the hydrogen recycle rate was adjusted to
33 obtain a hydrogen to naphtha feed molar ratio of 3.0.
34

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01 Liquid product was collected in the separator at 60°F. A
02 level control and valve allowed the separator to drain into
03 a debutanizer still which produced a C₅⁺ liquid product.

04 After feed introduction, the furnace temperature was rapidly
05 raised until the catalyst aromatization activity was able to
06 produce a liquid product comprising 42 wt. % aromatics. The
07 yield of liquid product was about 85 LV% on feed.
08 Thereafter as the catalyst deactivated temperatures were
09 raised to maintain constant aromatics in the liquid product.
10

11 In order to determine aromatization activity in terms of a
12 start of run temperature, the following procedure was used.
13 After an initial lineout period, the average catalyst bed
14 temperature was plotted against time to determine the
15 catalyst deactivation rate. Such plots are generally linear
16 and may be fitted by the least squares method. The slope of
17 the line is the catalyst deactivation rate and the start of
18 run temperature is defined as the zero time intercept. An
19 approximate eventual run length is estimated by making a
20 linear extrapolation to the end of run temperature. At end
21 of run, aromatics selectivity begins to decrease and
22 catalyst deactivation accelerates markedly. The end of run
23 temperature was expected to be 935°F for the feed and run
24 conditions above.
25

26 After startup, the pilot plant ran at constant LHSV, recycle
27 ratio, pressure, and aromatics for 658 hours. A least
28 squares fit of the reaction temperature data yielded a
29 fouling rate of 0.026°F/h and a start of run temperature of
30 855°F. Assuming an end of run temperature of 935°F, the
31 eventual run length would have been about 3100 hours if the
32 reaction conditions had remained unchanged.
33
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01 After 658 hours on-stream, reaction conditions were changed
02 in order to study process variable effects. The run
03 continued under various conditions for a total of
04 3810 hours. At the end of the run, the naphtha feed was
05 stopped and hydrogen circulation was continued while the
06 reactor furnace cooled to 500°F. The unit was then purged
07 with nitrogen and allowed to cool to ambient temperature.
08 Finally, the reactor was blocked off under nitrogen pressure
09 and the catalyst saved for a future regeneration.

11 EXAMPLE III

13 First Regeneration of the Catalyst

14 The reactor containing the catalyst from Example II was
15 reinstalled in the pilot plant, purged with nitrogen, and
16 heated to reaction temperature in hydrogen. The reforming
17 reaction was then resumed at the original space velocity,
18 pressure, and recycle ratio to determine catalytic activity.
19 After 84 hours on stream it was determined that and an
20 average catalyst temperature of 919°F was required to make a
21 C₅⁺ liquid product containing 42 wt. % aromatics. The
22 catalyst had therefore aged 74°F since the start of run in
23 Example II.
24

25 Hydrogen circulation continued while the naphtha feed was
26 stopped and the reactor furnace was cooled to 500°F. At
27 500°F, the sulfur converter/sorber reactor was bypassed and
28 blocked-in and the separator drained. Recycle gas
29 circulation continued overnight while the recycle loop was
30 purged with nitrogen and the reforming reactor cooled to
31 300°F.
32
33
34

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01 The carbon burn was initiated at 300°F and 95 psig by
02 introducing air and about sixty standard cubic centimeters
03 per minute of 1.0% oxygen/nitrogen blend to the recycle gas
04 stream and adjusting the air flow to maintain about
05 1.0% oxygen in the gas entering the reforming reactor. The
06 recycle gas rate was 1.3 standard liters per hour. The air
07 was dried with molecular sieves and metered through a mass
08 flowmeter. The oxygen/nitrogen blend was added to provide
09 enough off-gas for oxygen analysis. The molecular sieve
10 dryer remained in the recycle loop and moisture levels were
11 measured before and after the dryer. Reactor inlet oxygen
12 concentration was maintained at about 1.0% throughout the
13 burn. Water in the reactor inlet stream was less than
14 5 ppmv.

15
16 Upon introducing air an exotherm equal to about 20°F was
17 obtained at the front end of the catalyst bed. This was
18 attributed to the combustion of hydrocarbon vapors in the
19 recycle gas. The exotherm subsided after several hours.
20 The furnace temperature was held at 300°F for 22 hours then
21 raised to 500°F at a rate of 50°F/h. As the furnace
22 temperature was raised, the exotherm increased to about 25°F
23 and moved through the catalyst bed. The oxygen
24 concentration in the reactor effluent dropped to zero. By
25 the time the furnace temperature reached 500°F the exotherm
26 and oxygen consumption were decreasing again.

27
28 The furnace temperature was held at 500°F for 20.0 hours
29 then raised to 600°F at a rate of 50°F per hour. Again, the
30 burning of catalyst coke accelerated as temperature was
31 raised. The exotherm increased and oxygen in the reactor
32 effluent decreased. The exotherm peaked at about 10°F and
33 oxygen conversion peaked at about 30%. A short time after
34

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01 the furnace temperature reached 600°F, the burning again
02 subsided.

03 After holding at 600°F for 22.0 hours, the furnace
04 temperature was raised 50°F/h to 700°F. This time the peak
05 exotherm was less than 5°F. After 22.0 hours at 700°F, the
06 air and oxygen/nitrogen blend were shut-off. The recycle
07 gas dryer which was now loaded with water and carbon dioxide
08 was bypassed and a fresh dryer brought on-line. Gas
09 circulation continued while the recycle loop was purged with
10 nitrogen and the reforming reactor was cooled to 500°F.
11

12 Catalyst reduction was initiated at 500°F by depressuring to
13 70 psig and then pressuring up to 100 psig with hydrogen
14 while the compressor continued to operate. The makeup gas
15 was switched from nitrogen to hydrogen. The temperature was
16 held at 500°F for one-hour and then raised 4°F/h to 900°F.
17 The temperature was held at 900°F for 16 hours before
18 cooling to 800°F for naphtha feed introduction.
19

20

21

EXAMPLE IV

22

23

Catalyst Performance After First Regeneration

24

25

26

27

28

29

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32

33

34

After catalyst regeneration, the naphtha reforming reaction was resumed with the same conditions and feed used in Example II. Liquid product yields were the same as before regeneration and slightly better than with fresh catalyst. After 840 h on stream a least squares fit was made as before to determine the start of run temperature and deactivation rate. The start of run temperature was 859°F and the catalyst deactivation rate was 0.017°F/h. Thus, the catalyst activity had been restored to within 4°F of fresh catalyst. Surprisingly, the catalyst deactivation rate was

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01 significantly less than with fresh catalyst. The projected
02 run length was 4300 hours compared to 3100 hours for the
03 first cycle.

04
05 After determining start of run temperature and catalyst
06 deactivation rate, the liquid hourly space was increased to
07 3.0 and the furnace temperature was increased to obtain a
08 maximum catalyst bed temperature of 1025°F in order to
09 accelerate catalyst fouling. After 1464 hours at these
10 conditions, the catalyst had reached approximately end of
11 run activity and the liquid hourly space velocity was
12 reduced to the original value of 1.6. The average catalyst
13 bed temperature to produce a liquid product containing
14 42 wt % aromatics was then determined to be 939°F. The
15 catalyst had aged 80°F from the start of the second run
16 cycle.

17
18 EXAMPLE V

19
20 Second Regeneration of the Catalyst

21
22 At the conclusion of the run cycle described in Example IV,
23 the naphtha feed was stopped and the reforming reactor was
24 cooled to 500°F while continuing to circulate hydrogen. At
25 500°F, the recycle loop was purged with nitrogen, the sulfur
26 converter/sorber was taken off-line, and the separator was
27 drained. Purging continued while the reactor cooled to
28 300°F.

29
30 The catalyst was then regenerated following substantially
31 the same procedure used in Example III.

32
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EXAMPLE VICatalyst Performance Following Second Catalyst Regeneration

After the second regeneration, the reforming reaction was restarted with same conditions and feed used at the start of the first and second run cycles. After 660 hours, a least squares fit was again made to determine the start of run temperature and catalyst deactivation rate. The start of run temperature was determined to be 874°F and the catalyst deactivation rate was 0.012°F/h. The projected run length at these conditions was therefore about 5000 hours. The start of run temperature had declined 13°F from the start of previous run cycle, but the catalyst deactivation rate was again reduced so that projected run length had increased. The liquid C₅⁺ yield was the same as after the first regeneration.

EXAMPLE VIIRegeneration without Dryer

A coked catalyst from a 4700 hour pilot plant run was saved and later returned to service at the same conditions used in the previous examples. Prior to it's use, the catalyst had the same composition as the catalyst used in Example II. After 330 hours on-stream, the average catalyst bed temperature was 930°F and liquid product contained 42 wt. % aromatics. The yield of liquid product on feed was beginning to decline and was 85.5 LV%.

At this point the naphtha feed was stopped and the reactor cooled to 500°F in circulating hydrogen. At 500°F, the recycle loop was purged with nitrogen and the sulfur

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01 converter/sorber reactor and recycle gas dryer were bypassed
02 and the separator was drained. The pressure was adjusted to
03 85 psig. This time the carbon burn was started at 500°F.
04 Air and oxygen/nitrogen blend were added to the recycle gas
05 stream as in Examples III and V, but the oxygen content at
06 the reactor inlet was adjusted to 0.5% instead of 1.0%. The
07 dryer remained bypassed throughout the burn. There was
08 complete oxygen conversion and the exotherm was about 12°F.
09 After holding at 500°F for 1.5 hours, the furnace
10 temperature was raised 25°F/h to 700°F. Oxygen breakthrough
11 occurred when the furnace temperature reached about 640°F.
12 There was only a small amount of burning by the time the
13 furnace temperature reached 700°F and the exotherm was
14 negligible. Reactor inlet oxygen level was raised to 1.0%
15 and the temperature held at 700°F for 20 hours to complete
16 the burn. The exotherm during the final burn was less than
17 2°F.

18
19 Since the recycle gas dryer was bypassed, water built up in
20 the recycle gas during the burn until it reached saturation
21 levels in the separator. Moisture levels in the recycle gas
22 exceeded 2000 ppm well into the 700°F hold period.

23
24 After completing the carbon burn, the recycle loop was
25 purged with nitrogen and the reactor was cooled to 500°F
26 while recycle gas circulation continued. At 500°F the dryer
27 and the sulfur converter/sorber were put back on line. When
28 water in the recycle gas fell below 100 ppmv, the plant was
29 pressured up 100 psig with hydrogen to initiate catalyst
30 reduction. After an hour at 500°F, the reactor was heated
31 to 900°F at rate of 10°F/h. The reactor was held at 900°F
32 until the moisture content of the reactor effluent was less
33 than 100 ppm then cooled to 800°F for feed introduction.

34

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EXAMPLE VIIICatalyst Performance after Regenerating without a Dryer

After the catalyst regeneration in Example VII, the naphtha feed was restarted and the reforming reaction resumed for 590 hours. The feed and the run conditions were the same as in Example II. Catalyst performance was not as good as obtained in Examples II, IV, or VI. The start of run temperature was 868°F and the fouling rate was 0.031°F/h. The projected run length was therefore only about 2100 hours.

EXAMPLE IXRegeneration with Dryer

The regeneration procedure of Example VIII was repeated with another coked catalyst sample except that the recycle gas drier was employed during the carbon burn and consequently the reactor inlet moisture levels were always less than 5 ppm. The catalyst composition prior to its use as a reforming catalyst was the same as that used in Examples II and VII.

EXAMPLE XCatalyst Performance After Regeneration with Dryer

The catalyst regenerated in Example IX was tested with the same run conditions and feed as in Example VIII. After 576 hours on stream, the start of run temperature was 862°F and catalyst deactivation rate was 0.019°F/hr. The

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01 projected run length was 3800 hours compared to 2100 in
02 Example VIII.

03 The results of from Examples I to X are summarized in
04 Table 1 below.
05

06 Table 1

08	09	10	11	12	13	14
			Start of		Deactivation	Projected
			Run		Rate °F/h	Run (hours)
			Temp. °F			
11	Fresh Catalyst	II	855		0.026	3100
12	First					
13	Regeneration	II - IV	859		0.017	4100
14	Second					
15	Regeneration	V - VI	874		0.012	5000
16	Regeneration					
17	without Dryer	VII - VIII	868		0.031	2100
18	Regeneration					
19	with Dryer	IX - X	862		0.019	3800
20						

21 The table clearly shows that a controlled low temperature
22 carbon-burn regeneration procedure restores most of the
23 activity present at the start of the previous run cycle and
24 that catalyst deactivation rates are significantly reduced,
25 such that several cycles are possible before there is a need
26 for platinum redispersion. The results further show the
27 advantage in using a dryer to reduce the water content of
28 the recycle gas during the carbon burn. These results are
29 surprising in view of the prior art and afford the
30 opportunity to increase cycle length and avoid the use of
31 corrosive and sometimes highly toxic halogen compounds
32 during regeneration.
33
34

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EXAMPLE XIRegeneration Procedure for a Large-Scale Plant

01
02
03
04
05 Allowing for differences in the exotherm as compared to a
06 pilot plant, a commercial unit with four reactors in series
07 is regenerated as follows. Naphtha feed is withdrawn and
08 hydrogen is circulated at high temperature to strip
09 hydrocarbon from the catalyst. The separator and knockout
10 drums are periodically drained of hydrocarbon. Hydrogen
11 circulation is continued while the reactors are cooled to
12 about 420°F. At 420°F, the recycle loop is purged with
13 nitrogen and low points are checked for liquid hydrocarbons.
14 After periodic draining shows that little or no hydrocarbon
15 liquids are being collected, it is advantageous to switch to
16 a fresh recycle gas dryer which is substantially free of
17 hydrocarbons and water. If there is a recycle gas sulfur
18 converter/sorber, it will be bypassed at this point.

19
20 When the reactor inlets are at 420°F and the level of
21 combustibles in the recycle gas is less than 2.0%, air is
22 introduced to the recycle gas stream. The oxygen level at
23 the first reactor inlet is adjusted to 0.5%. The burning of
24 residual combustibles in the recycle gas consumes all the
25 oxygen and results in an 80 to 125°F exotherm across the
26 first reactor. Eventually, the vapor-phase combustibles are
27 consumed and the burn-wave moves through the reactor chain.
28 After oxygen breakthrough occurs and the exotherm subsides,
29 furnace temperatures are raised at rate of about 25°F/h
30 until peak catalyst bed temperature reaches 700°F. The
31 total exotherm at this point is less than about 20°F. When
32 oxygen conversion across the reactor train drops to less
33 than 10%, the oxygen concentration at the reactor inlet is
34 raised to 1.0 to 4.0% and the furnace temperatures are

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01 adjusted to maintain the peak catalyst bed temperatures as
02 close to 700°F as possible.

03
04 Temperatures are maintained at 700°F for 12 to 24 hours
05 before the air makeup is stopped. The recycle loop is then
06 purged with nitrogen and cooled to 500°F. At 500°F the
07 recycle gas dryers are switched again and the sulfur
08 converter/sorber is brought back on-line. About twice the
09 stoichiometric amount of hydrogen needed for reduction of
10 the catalyst is fed into the unit over a period of about an
11 hour. The unit is then partially depressured and pressured
12 up with hydrogen to adjust the hydrogen to nitrogen ratio to
13 about one-to-four. Higher hydrogen to nitrogen ratios can
14 result in excessive ammonia formation, which is catalyzed by
15 the iron particles present in the reactor tubes. The
16 temperature is held at 500°F for about an hour then raised
17 10°F/h to 900°F. The hydrogen/nitrogen ratio is maintained
18 by adjusting hydrogen and nitrogen makeup rates. The
19 temperature is held at 900°F for at least 12 hours. When
20 water in the fourth reactor effluent is less than 100 ppm,
21 the temperature is dropped to 700°F or lower to await feed
22 introduction.

23 EXAMPLE XII

24 Reforming With A Silicalite Catalyst/Catalyst Coking

25
26
27 A silicalite catalyst was produced by impregnating a dried
28 synthesized Silicalite powder to give 1% Pt on the
29 Silicalite powder, then mixing this with SAPO-11 powder to
30 produce a finished catalyst consisting of 25% wt SAPO-11 and
31 75% wt Pt Silicalite.
32
33
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01 This catalyst was used to convert hexane containing feeds to
02 aromatics. The feed composition are listed in Table XI.
03 The conversion conditions used were a pressure of 30 PSIG, a
04 WHSV of 0.72, a hydrogen to hydrocarbon ratio of seven to
05 one, with the catalyst temperatures ranging from 880 to
06 1000° F to maintain a high product benzene level and adjust
07 for fouling.

08
09 EXAMPLE XIII

10
11 Regeneration Of Silicalite Catalyst

12
13 The catalyst of Example XII was repeatedly coked and
14 regenerated. The regeneration conditions included treating
15 the catalyst with low concentrations (0.5 to 2.0 wt%) of
16 oxygen at 30 to 100 psig at a GHSV of 923.

17
18 The regeneration temperature was varied over the range of
19 450 to 680°F. Regenerations below about 500°F for 16 to
20 24 hours were not successful in producing a catalyst having
21 an activity (as measured by hexane conversion) or a
22 selectivity (as measured by the wt% benzene in the product)
23 similar to fresh catalyst. At regeneration temperatures
24 between 550 and 680°F, aromatization activity was restored
25 to about that of the start of the run cycle.

26
27 Table 2, below shows the regeneration temperatures and times
28 for several of these regenerations, along with the activity
29 and selectivity results. The regenerated catalyst was
30 able to maintain product benzene levels of about 40 wt.%,
31 for greater than 1000 hours between regenerations.

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TABLE 2

REGENERATION CONDITIONS				SELECTIVITY AND ACTIVITY RESULTS*				
Regen. No.	Temp. °F	Hours	O ₂ Level %	Pressure psig #	Before Regen.		After Regen.	
					Hexane Conversion	Product wt. % Benzene	Hexane Conversion	Product wt. % BZ
10	600 630	72.0 46.7	0.5 1.0	30 100	55	14	74	41
11	600 630	46.8 3.6	1.0 1.0	100 100	82	27	68	39
12	600 630 660	26.3 65.3 119.2	1.0 1.0 1.0	100 100 100	86	8	72	41
13	600 630 660 680	66.6 24.9 30.9 43.9	1.0 1.0 1.0 1.0	100 100 100 100	59	24	98	39
0	Fresh Catalyst at 21 Hrs. on Stream				98 (3)	42 (3)		
								1000+ (5)

* Conversion Conditions: 30 psig, VHSV = 0.72, Catalyst Temp. 880°F to 1000°F

(1) Utilizing Feed B (Table 3)

(2) At constant (40%) aromatization activity.

(3) Utilizing Feed A (Table 3)

(4) BZ = Benzene

(5) Run was voluntarily terminated; catalyst remained active.

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TABLE 3

FEED COMPOSITION

<u>COMPOUND</u>	FEED A	FEED B
	LIGHT NAPATHA	MODEL FEED
	<u>wt. %</u>	<u>wt. %</u>
Total C ₅	16.1	0.0
Total C ₆	49.7	70.0
Total C ₇	34.2	24.0
N-C ₆	12.5	70.0
Methyl Cyclohexane	5.9	6.0

Feed A used for start of run.

Feed B used for regeneration studies.

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01 WHAT IS CLAIMED IS:

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1. A process for regenerating a coke contaminated reforming catalyst comprising platinum on a molecular sieve, said process consisting essentially of contacting said catalyst with a halogen-free oxygen-containing gas at a temperature of less than 780°F for a sufficient period of time such that the catalyst aromatization activity is restored to within 20°F of the activity said catalyst possessed at the start of the previous run cycle.
2. The process as recited in Claim 1 wherein the oxygen content of the oxygen containing gas is from between about 0.1 to about 21.0 mole % oxygen.
3. The process as recited in Claim 1 wherein the oxygen content of the oxygen containing gas is from about 0.2 to about 4.0 mole %.
4. The process as recited in Claim 1 wherein the molecular sieve is a large-pore zeolite.
5. The process as recited in Claim 4 wherein the large-pore zeolite is selected from the group consisting of type-X, type-Y, type L, beta zeolite, and mordenite.
6. The process as recited in Claim 4 wherein the large-pore zeolite is type-L zeolite.
7. The process as recited in Claim 1 wherein the molecular sieve is silicalite.

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- 01 8. The process as recited in Claim 4 wherein the zeolite
02 further comprises an alkaline earth metal.
- 03
04 9. The process as recited in Claim 5 wherein the zeolite
05 further comprises boron.
- 06
07 10. The process as recited in Claim 1, 6 or 7 wherein the
08 catalyst is bound with a support matrix comprising
09 alumina, silica or mixtures thereof.
- 10
11 11. The process as recited in Claim 1 further comprising
12 reducing the regenerated catalyst by contacting the
13 catalyst with a gaseous stream containing hydrogen at a
14 initial temperature from 300°F to 700°F.
- 15
16 12. The process as recited in Claim 11 further comprising
17 raising the temperature of the gaseous
18 hydrogen-containing stream to between 800°F and 1000°F
19 to complete the dryout and reduction.
- 20
21 13. The process as recited in Claim 11 wherein the carbon
22 burn is initiated at a temperature of less than 500°F.
- 23
24 14. The process as recited in Claim 13 wherein the
25 temperature is escalated during the carbon burn in a
26 slow ramping fashion.
- 27
28 15. The process as recited in Claim 13 wherein the
29 temperature is escalated during the carbon burn in a
30 stepwise fashion.
- 31
32 16. The process as recited in Claim 1 wherein the peak
33 catalyst temperature during the carbon burn step is
34 between 600°F and 750°F.

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- 01 17. The process as recited in Claim 11 wherein prior to
02 reducing the catalyst, the catalyst is purged with an
03 inert gaseous stream.
- 04 18. The process as recited in Claim 1 further comprising
05 drying at least a portion of the combustion gas
06 resulting from the contacting of the catalyst with the
07 oxygen containing gas and then recycling the dried
08 combustion gas to the reactor.
09
- 10 19. The process as recited in Claim 6 further comprising
11 reducing the regenerated catalyst by contacting the
12 catalyst with a gaseous stream containing hydrogen at a
13 initial temperature from 300°F to 700°F.
14
- 15 20. The process as recited in Claim 6 wherein the carbon
16 burn is initiated at a temperature of less than 500°F.
17
- 18 21. The process as recited in Claim 6 wherein the peak
19 catalyst temperature during the carbon burn step is
20 between 600°F and 750°F.
21
- 22 22. The process as recited in Claim 6 further comprising
23 drying at least a portion of the combustion gas
24 resulting from the contacting of the catalyst with the
25 oxygen containing gas and then recycling the dried
26 combustion gas to the reactor.
27
- 28 23. A process for regenerating a coke deactivated reforming
29 catalyst, comprising :
30
- 31 (a) contacting a coke-deactivated L-zeolite catalyst
32 with a halogen-free oxygen-containing gaseous
33 stream at a temperature of between 300 and 780°F
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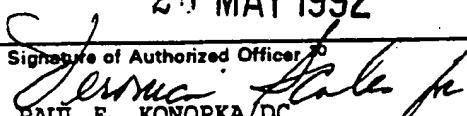
-41-

- 01 and at an inlet water concentration of less than
02 100 ppmv; and
03
04 (b) reducing the catalyst resulting from step (a) by
05 contacting the catalyst with a hydrogen containing
06 gas.
07
08 24. The process as recited in Claim 23 further comprising
09 the step of purging the catalyst resulting from step
10 (a) with a gaseous stream comprising nitrogen prior to
11 the reduction step (b).
12
13 25. A reforming process comprising contacting a hydrocarbon
14 stream during a run with a platinum containing
15 molecular sieve catalyst under reforming conditions and
16 regenerating said catalyst by the process as recited
17 Claim 1.
18
19 26. A reforming process wherein a reforming catalyst is
20 regenerated for at least two cycles by the process as
21 recited in Claim 1.
22
23 27. The process as recited in Claim 1 wherein the catalyst
24 is continuously withdrawn from reactors for
25 regeneration in a separate vessel, and returned to the
26 reactors.
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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/01001

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): C10G 35/095, C10G 35/09, B01J 29/38, B01J 23/96 US CL : 208/138,140 502/38,50,52		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	208/138,140 502/38,50,52	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category*	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 3,836,597 (SIE) 17 SEPTEMBER 1974	1-5,10-21
Y	US, A, 3,836,597 (SIE) 17 SEPTEMBER 1974 (SEE COLUMN 3, LINE 74 TO COLUMN 4, LINE 36)	6-9,22-27
Y	US, A, 4,600,700 (McHALE) 15 JULY 1986 (SEE COLUMN 4, LINES 30-68 AND COLUMN 1, LINES 12-16)	1-27
Y,P	US, A, 5,073,529 (MILLER ET AL.) 17 DECEMBER 1991 (SEE COLUMNS 7,8 AND 9)	1-27
A	US, A, 4,631,123 (BUSS ET AL.) 23 DECEMBER 1986 (SEE ENTIRE DOCUMENT)	1-27
A	US, A, 4,650,565 (JACOBSON ET AL.) 17 MARCH 1987	1-27
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²		Date of Mailing of this International Search Report ²
16 APRIL 1992		25 MAY 1992
International Searching Authority ¹		Signature of Authorized Officer ¹⁰
ISA/US		 PAUL E. KONOPKA/DC